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(54) **PROCESS FOR THE PREPARATION OF NEEDLE COKE FOR GRAPHITE ELECTRODES**

(57) This invention relates to a process for preparing needle coke for graphite electrodes which comprises treating coal-tar or petroleum-based needle coke with a solution or suspension of iron oxide or a compound forming iron oxide by undergoing reaction or decomposition upon heating with coke until adhesion of 0.1 to 15% by weight of the iron compound to the needle coke before kneading with binder pitch and then heat treating at 300 to 1,600°C or calcining at 1,200 to 1,600 °C. The process of this invention makes it possible to prepare needle coke with reduced puffing during the graphitization, increased yield during the graphitizing step and improved product properties such as strength regardless of whether the raw material coke is derived from coal or petroleum.

**EP 1 065 189 A1**

**Description**Technical Field

- 5 **[0001]** This invention relates to a process for preparing needle coke useful as raw material for the manufacture of graphite electrodes.

Background Technology

- 10 **[0002]** Coke useful for artificial graphite electrodes, namely needle coke, is obtained by converting heavy oil such as coal tar-derived pitch and petroleum-derived pitch into green coke by delayed coking and calcining the green coke. Artificial graphite electrodes are manufactured by adjusting the particle size of needle coke to a given size distribution, kneading with binder pitch, forming by extrusion, baking, impregnating a pitch, baking secondarily, repeating the foregoing procedure several times if necessary, and graphitizing. The graphitization consists of a heat treatment at 2,500 to 3,000 °C and an LWG furnace (direct current-carrying type) is generally used in this step.

15 **[0003]** However, the temperature rises rapidly when graphitization is effected in this LWG furnace and, as a result, gases are generated at a higher rate and a phenomenon of abnormal volume expansion called puffing tends to occur readily.

- 20 **[0004]** Puffing reduces the density of electrodes and, in extreme cases, damages electrodes and studies have been carried on to develop puffing inhibitors and make needle coke with a low degree of puffing.

- [0005]** Puffing is considered to occur when sulfur is released at a temperature in the range of 1,700 to 2,000 °C where graphitization begins and compounds such as iron oxide ( Japanese patent JP55- 110190(A1)), nickel and related compounds (JP60- 190491(A1)), and titanium oxide (JP02-51409(A1)) have been disclosed as puffing inhibitors, that is, compounds capable of forming sulfides such as iron sulfide by temporarily trapping the released sulfur and decomposing at a higher temperature thereby shifting the timing of sulfur release to a higher temperature. It has been confirmed that the effect of iron oxide varies with the kind of raw material coke, excellent on petroleum-based coke but poor on coal tar-based coke.

- 30 **[0006]** JP02-92814(A1) discloses a process for uniformly dispersing an iron compound as inhibitor inside the pores of coke wherein coke is impregnated with a solution of solvent-soluble iron sulfate or iron nitrate in water, alcohol and the like or with a suspension of fine powders of iron oxide, drying the impregnated coke to drive off the water or the alcohol, mixing the dried coke with binder pitch, and graphitizing the mixture. When the impregnated coke is merely dried, however, the inhibitor impregnating the coke releases moisture or decomposes into gases to cause such problems as defective and low-strength electrodes.

- 35 **[0007]** On the other hand, JP53-35801(B1) discloses a process for preparing low-puffing needle coke by carrying out the first-stage calcination of green coke at a temperature lower than the one normally used, say in the range of 600 to 1,000 °C, cooling once, and then carrying out the second-stage calcination at a temperature in the range of 1,200 to 1,500 °C. However, carrying out the calcination in multiple steps runs into a problem of increased consumption of thermal energy and is economically questionable unless sufficient reduction of puffing is obtained.

- 40 **[0008]** In consequence, an object of this invention is to provide low-puffing needle coke useful for graphite electrodes which is capable of improving the yield and properties of graphite electrodes.

**[0009]** Another object of this invention is to provide a process for preparing needle coke useful for graphite electrodes which is capable of sufficiently controlling the puffing of not only petroleum-based needle coke but also coal tar-based coke without incurring heavy production cost.

- 45 **[0010]** The present inventors have conducted an intensive study to solve the problems involved in the aforementioned objects, found that the effect of controlling puffing can be increased markedly by using as a puffing inhibitor at least one kind of iron compound selected from iron oxide and compounds forming iron oxide either by reaction or decomposition upon heating, impregnating needle coke or calcined coke of intermediate stage with a solution or suspension of such puffing inhibitor, and heating at a temperature sufficiently higher than the normal drying temperature, and completed this invention.

Disclosure of the Invention

- 55 **[0011]** Accordingly, this invention relates to a process for preparing needle coke useful for graphite electrodes which comprises treating needle coke with a solution or suspension of at least one kind of iron compound selected from iron oxide and compounds forming iron oxide by either reaction or decomposition upon heat treatment with coke until adhesion of 0.1 to 15% by weight of the iron compound to the needle coke prior to kneading with binder pitch and submitting to heat treatment at a temperature in the range of 300 to 1,600 °C.

**[0012]** In addition, this invention is concerned with a process for preparing needle coke by calcining in two or more

stages the green coke manufactured by delayed coking and relates to a process for preparing needle coke useful for graphite electrodes which comprises carrying out the fore-stage calcination of the green coke at a temperature in the range of 600 to 1,000 °C to calcined coke of intermediate stage, treating it with a solution or suspension of at least one kind of iron compound selected from iron oxide and compounds forming iron oxide by either reaction or decomposition upon heat treatment with coke until adhesion of 0.1 to 15% by weight of the iron compound, and carrying out the rear-stage calcination at a temperature in the range of 1,200 to 1,600 °C.

**[0013]** In this invention, compounds forming iron oxide are preferably at least one kind of iron compound selected from a group of iron sulfate, iron chloride, iron nitrate, iron carbonate, iron alum, iron carbonyl, iron acetate, iron citrate, and cyclopentadienyliron.

**[0014]** This invention will be described in detail below.

**[0015]** Coke to be used in this invention is needle coke or coke of intermediate stage obtained by calcining green coke manufactured by delayed coking of heavy oils composed of one or both of petroleum- and coal tar-derived pitches.

**[0016]** The calcining temperature is in the range of about 1,000 to 1,600°C, preferably about 1,200 to 1,500°C, in one-stage calcination while it is in the range of about 600 to 1,000 °C in the fore stage and in the range of about 1000 to 1,600 °C, preferably about 1,200 to 1,500 °C, in the rear stage in two-stage calcination. It is possible to carry out the calcination in three stages or more and, in such a case, the calcining temperature is raised successively one stage after another.

**[0017]** Where calcined needle coke is used, the calcination may be carried out in one stage or multiple stages without ill effect but it must be carried out before kneading with binder pitch.

**[0018]** Where calcined coke of intermediate stage is used, the calcination may be carried out either in two stages or in three stages or more without ill effect and it is preferable for the coke in question to have been calcined in the temperature range of about 600 to 1,000 °C in the fore stage. Here also, the calcination must be carried out before kneading with binder pitch.

**[0019]** The aforementioned needle coke or calcined coke of intermediate stage is impregnated with a solution or suspension of an iron compound while the temperature of coke is preferably kept below 100°C.

**[0020]** Iron compounds to be used in this invention are iron oxide or those compounds which react or decompose upon heating to form iron oxide and they are used dissolved or suspended in a solvent such as water, alcohol, acetone and hydrocarbon oil, preferably in water. When coke is impregnated with such iron compound in solution or suspension, the compound adheres not only to the surface of coke but also to the inside of pores of coke with the resultant enhanced effect as inhibitor. Therefore, where a solvent-insoluble iron compound such as iron oxide and iron hydroxide is used, it is advantageously applied as a suspension with such particle diameter as to allow intrusion into the pores of needle coke. Concretely, the average particle diameter is 100 μ m or less, preferably 10 μ m or less.

**[0021]** In order to ensure sufficient adhesion of iron compounds not only to the surface but also to the inside of pores, it is preferable to use a group of iron sulfate, iron chloride, iron nitrate, iron carbonate and iron alum which are readily soluble in water and another group of iron carbonyl, iron acetate, iron citrate and cyclopentadienyliron which are readily soluble in organic solvents such as alcohol and benzene and apply them as solutions in such solvents. A suspension of iron oxide in a solvent with the particle diameter sufficiently reduced to allow entrance into pores of coke is also desirable.

**[0022]** The amount of adhering iron compound is 0.1 to 15% by weight, preferably 0.5 to 10% by weight, based on coke. Any amount short of this range does not produce a sufficient effect for reducing puffing in practice while any amount in excess of this range produces no more noticeable effect and besides the ash content exerts an undesirable influence on the properties of finished electrodes. Here, the amount of adhering iron compound refers to the amount calculated as iron oxide.

**[0023]** Needle coke or calcined coke of intermediate stage is impregnated with a solution or suspension of iron compound, dried and then submitted to heat treatment or rear-stage calcination.

**[0024]** In the cases where calcined needle coke is impregnated, heat treatment is effected at a temperature in the range of 300 to 1,600°C, preferably 300 to 1,500 °C, more preferably 500 to 1,000 °C.

**[0025]** The conditions for this heat treatment such as temperature and length of time are preferably so chosen that iron compounds containing water of crystallization are freed of the water and iron compounds other than iron oxide are converted substantially wholly to iron oxide. In particular, where iron compounds undergo decomposition or reaction to yield iron oxide accompanied by generation of gases, the conditions are so chosen as to maximize the occurrence of such decomposition and reaction. The temperature of heat treatment is preferably set at 300°C or more as water of crystallization is difficult to come off below 300°C or, more preferably, at 500°C or more to allow iron compounds to react with oxygen present in the atmosphere or to cause iron compounds themselves to decompose. On the other hand, heat treatment at a temperature in excess of 1,600°C is not economical because the effect for controlling puffing reaches a saturation point and does not increase any more in response to a further input of heat energy. It is preferable to effect the heat treatment in a reducing atmosphere.

**[0026]** In the cases where calcined coke of intermediate stage is impregnated with a solution or suspension of iron

compounds, the impregnated coke is dried and submitted to the rear-stage calcination. The rear-stage calcination is preferably carried out at a temperature higher than that for the fore-stage calcination and, in case the temperature for the latter is in the range of 600 to 1,000 °C, the temperature for the former is in the range of about 1,000 to 1,600 °C, preferably about 1,000 to 1,500 °C, more preferably about 1,200 to 1,500 °C. Here, the fore-stage calcination refers to the calcination carried out immediately before the impregnation while the rear-stage calcination refers to the calcination carried out after the impregnation.

**[0027]** The aforementioned heat treatment or the rear-stage calcination effected after the impregnation with iron compounds prevents the formation of defects in electrodes caused by moisture released from iron compounds or the decrease in bulk density of electrodes caused by gases resulting from the decomposition of iron compounds during calcination in the course of the manufacture of electrodes.

**[0028]** For the preparation of graphite electrodes from needle coke obtained in the aforementioned manner, the needle coke is pulverized, adjusted to a given particle size distribution, kneaded with binder pitch, formed by extrusion, baked, impregnated with pitch, baked secondarily, with repetition of this procedure several times as needed, and finally graphitized by heating at a temperature in the range of about 2,500 to 3,000 °C. Iron oxide is often added as puffing inhibitor during kneading with binder pitch, but this addition may be omitted in the procedure of this invention as iron oxide is already present in coke. Nevertheless, the addition of iron oxide here helps to produce a still more enhanced effect of reducing puffing.

#### Best Mode for Carrying out the Invention

**[0029]** This invention will be described with reference to examples below. Needle cokes obtained in the examples and comparative examples are measured for puffing and bulk density (BD) in accordance with the following methods.

#### (Method of measuring puffing )

**[0030]** Coke is pulverized, sized (8 ~ 16 mesh, 40%; 48 ~ 200 mesh, 35%; 200 mesh and less; 25%), kneaded with 30% (the percentage to the gross amount) of binder pitch at 160°C for 20 minutes, and molded into a test piece measuring 20 mm  $\phi$   $\times$  100 mm. The test piece is baking up to 900 °C in a baking furnace, impregnated with pitch, baked secondarily again at 900 °C and used as sample for the measurement of puffing. The sample is heated to 2,500 °C at a rate of 10°C/min and puffing is expressed in terms of the maximum degree of elongation observed from 1,500°C to 2,500 °C.

#### (Method of measuring bulk density after graphitization )

**[0031]** The volume of the test piece is calculated from its diameter and length and also the test piece is weighed. The bulk density is calculated by dividing the weight with the volume.

#### Example 1

**[0032]** Green coke manufactured from coal tar-derived heavy oil by delayed coking was calcined to give coal tar-based needle coke.

**[0033]** The needle coke (3 kg) was impregnated with an 8wt% aqueous solution of iron sulfate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150°C, and then heat-treated at 900 °C to give needle coke for graphite electrodes.

#### Example 2

**[0034]** The needle coke (3 kg) of Example 1 was impregnated with a 12wt% aqueous solution of iron nitrate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150 °C, and then heat-treated at 900 °C to give needle coke for graphite electrodes.

#### Example 3

**[0035]** The needle coke (3 kg) of Example 1 was impregnated with a 13wt% aqueous solution of iron alum until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150°C, and then heat-treated at 900 °C to give needle coke for graphite electrodes.

## Example 4

[0036] The needle coke (3 kg) of Example 1 was impregnated with an 8wt% aqueous solution of iron acetate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150 °C, and then heat-treated at 900 °C to give needle coke for graphite electrodes.

## Comparative Example 1

[0037] The needle coke (3 kg) of Example 1 was impregnated with an 8wt% aqueous solution of iron sulfate until adhesion of 750 g of the solution, left standing for 30 minutes and dried at 150°C to give needle coke for graphite electrodes. The heat treatment was not carried out.

## Example 5

[0038] The needle coke (3 kg) of Example 1 was impregnated with an 8wt% aqueous solution of iron sulfate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150 °C, and then submitted to heat treatment at 900 °C to give needle coke for graphite electrodes.

[0039] The coke for graphite electrodes thus obtained was kneaded with binder pitch while adding 1 part by weight of iron oxide to 100 parts by weight of the coke and the test piece and sample were prepared as in Example 1 for measurement of puffing and bulk density after graphitization.

## Example 6

[0040] Green coke manufactured from petroleum-derived heavy oil by delayed coking was calcined to give petroleum-derived needle coke.

[0041] The needle coke was impregnated with an 8wt% aqueous solution of iron sulfate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150°C, and then heat-treated at 900 °C to give needle coke for graphite electrodes.

## Comparative Example 2

[0042] The needle coke used in Example 1 which had been obtained by calcining the green coke was measured for puffing and bulk density after graphitization.

## Comparative Example 3

[0043] The test piece and sample were prepared as in Comparative Example 2 except adding 1 part by weight of iron oxide to 100 parts by weight of the coke and measured for puffing and bulk density after graphitization.

## Comparative Example 4

[0044] The petroleum-derived needle coke of Example 6 which had been obtained by calcining the green coke was measured for puffing and bulk density after graphitization.

[0045] The test conditions and the results of measurements of Examples 1 to 6 are shown in Table 1 and those of Comparative Examples 2 to 4 in Table 2.

[0046] The amount of adhering iron compound is calculated by the following equation:

$$\text{Amount of adhering iron compound (wt\%)} = (C - A)/B \times 100$$

wherein A is the mass of ash when the needle coke before impregnation with the iron compound is incinerated at 800 °C, B is the mass of the needle coke after impregnation with the iron compound and heat treatment (or drying where heat treatment is omitted), and C is the mass of ash when the needle coke of mass B is incinerated at 800 °C.

Table 1

	Example	Example	Example	Example	Comparative example	Example	Example
	1	2	3	4	1	5	6
Needle coke	Coal tar based	Coal tar based	Coal tar based	Coal tar based	Coal tar based	Coal tar based	Petroleum based
Iron compound	Iron sulfate	Iron nitrate	Ammonium iron sulfate	Iron acetate	Iron sulfate	Iron sulfate	Iron sulfate
Heat treatment temperature(°C)	900	900	900	900	-	900	900
Amount of adhering iron compound(wt%)	1.0	1.0	0.9	0.9	1.0	1.0	0.9
Addition of iron compound during kneading	None	None	None	None	None	1 part by weight	None
Puffing	1.08	0.97	1.07	1.05	1.13	0.90	0.8
Graphitized bulk density	1.58	1.59	1.56	1.57	1.54	1.61	1.60

Table 2

	Comparative example	Comparative example	Comparative example
	2	3	4
Needle coke	Coal tar based	Coal tar based	Petroleum based
Iron compound	-	-	-
Heat treatment temperature(°C)	-	-	-
Ash content (wt%)	0.08	0.08	0.10
Addition of iron compound during kneading	None	1 part by weight	None
Puffing	1.91	1.48	1.18
Graphitized bulk density	1.53	1.56	1.58

## Example 7

- [0047]** Green coke prepared by delayed coking of coal-derived heavy oil was calcined at 800°C to give calcined coke of intermediate stage which was used in this example. To 3 kg of this calcined coke was added 750 g of an 8wt% aqueous solution of iron sulfate, the mixture was left standing for 30 minutes, dried at 150 °C, and then calcined at 1,400°C to give coke for graphite electrodes.

## Example 8

**[0048]** The calcined coke (3 kg) of Example 7 was impregnated with a 12wt% aqueous solution of iron nitrate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150°C, and then calcined at 1,400°C to give coke for graphite electrodes.

## Example 9

**[0049]** The calcined coke (3 kg) of Example 7 was impregnated with a 13wt% aqueous solution of iron alum until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150°C, and then calcined at 1,400°C to give coke for graphite electrodes.

## Example 10

**[0050]** The calcined coke (3 kg) of Example 7 was impregnated with an 8wt% aqueous solution of iron acetate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150°C, and then calcined at 1,400°C to give coke for graphite electrodes.

## Example 11

**[0051]** The calcined coke of Example 7 was impregnated with an 8wt% aqueous solution of iron sulfate until adhesion of 750 g of the solution, left standing for 30 minutes, dried at 150°C, and then calcined at 1,400 °C to give coke for graphite electrodes.

**[0052]** The test piece and sample were prepared as in Example 7 from the coke for graphite electrodes thus obtained except adding 1 part by weight of iron oxide to 100 parts by weight of the coke during kneading with binder pitch and measured for puffing and bulk density after graphitization.

## Comparative Example 5

**[0053]** The calcined coke of Example 7 was further calcined at 1,400 °C without impregnation with iron compound to give needle coke for graphite electrodes.

## Comparative Example 6

**[0054]** The test piece and sample were prepared as in Comparative Example 5 from the coke for graphite electrodes obtained in Comparative Example 5 except adding 1 part by weight of iron oxide to 100 parts by weight of the coke during kneading with binder pitch and measured for puffing and bulk density after graphitization.

**[0055]** The test conditions and the results of measurement of Examples 7 to 11 and Comparative Examples 5 and 6 are shown in Table 3.

Table 3

	Example	Example	Example	Example	Example	Compara- tive exam- ple	Compara- tive exam- ple
	7	8	9	10	11	5	6
Iron com- pound	Iron sulfate	Iron nitrate	Ammonium iron sulfate	Iron acetate	Iron sulfate	-	-
Amount of adhering iron com- pound(wt%)	0.9	0.9	0.8	1.1	1.0	-	-

Table 3 (continued)

	Example	Example	Example	Example	Example	Compara- tive exam- ple	Compara- tive exam- ple
5	7	8	9	10	11	5	6
10	Addition of iron com- pound dur- ing kneading	None	None	None	1 part by weight	None	1 part by weight
	Puffing	1.07	0.87	0.97	1.15	0.77	1.80
15	Graphitized bulk density	1.60	1.61	1.57	1.57	1.61	1.55
						1.41	1.58

Industrial Applicability

20 **[0056]** Needle coke for graphite electrodes obtained by the process of this invention effectively controls puffing in the graphitization step and raises the yield of electrodes and still more improves the product properties such as strength in the manufacture of electrodes. Also, the process of this invention is highly useful as it is applicable not only to petroleum-based needle coke but also to coal-based needle coke.

**25 Claims**

1. A process for preparing needle coke for graphite electrodes which comprises treating needle coke with at least one kind of iron compound selected from iron oxide and compounds forming iron oxide by undergoing reaction or decomposition upon heating with coke in the state of a solution or suspension until adhesion of 0.1 to 15% by weight of the iron compound to the needle coke before kneading with binder pitch and then heattreating at a temperature in the range of 300 to 1,600 °C.
2. In a process for preparing needle coke by calcining in two or more stages the green coke manufactured by delayed coking, a process for preparing needle coke for graphite electrodes which comprises calcining the green coke at a temperature in the range of 600 to 1,000 °C in the fore stage to give calcined coke of intermediate stage, treating said calcined coke with at least one kind of iron compound selected from iron oxide and compounds forming iron oxide by undergoing reaction or decomposition upon heating with coke in the state of a solution or suspension until adhesion of 0.1 to 15% by weight of the iron compound to said calcined coke before kneading with binder pitch and then calcining at a temperature in the range of 1,200 to 1,600 °C in the rear stage.
3. A process for preparing needle coke for graphite electrodes as described in claim 1 or 2 wherein said compounds forming iron oxide are at least one kind of iron compound selected from a group of iron sulfate, iron chloride, iron nitrate, iron carbonate, iron alum, iron carbonyl, iron acetate, iron citrate and cyclopentadienyliron.



REVISED  
VERSION

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/00316

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl<sup>6</sup> C04B35/52, C01B31/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>6</sup> C04B35/52, C01B31/00-31/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999

Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 63-288964, A (Toyo Carbon Co., Ltd.), 25 November, 1988 (25. 11. 88) (Family: none)	1-3
A	JP, 2-92814, A (Showa Denko K.K.), 3 April, 1990 (03. 04. 90) (Family: none)	1-3
A	JP, 53-35801, B2 (Koa Oil Co., Ltd.), 29 September, 1978 (29. 09. 78) & US, 4100265, A	1-3

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

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- "E" earlier document but published on or after the international filing date
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Date of the actual completion of the international search  
5 February, 1999 (05. 02. 99)

Date of mailing of the international search report  
16 February, 1999 (16. 02. 99)

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